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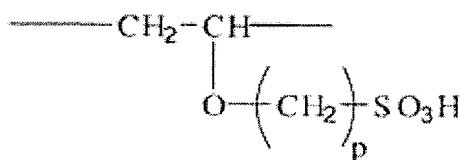
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(54) SOLID POLYMER ELECTROLYTE FILM FOR FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid polymer electrolyte film with excellent durability at low cost.

SOLUTION: This solid polymer electrolyte film has the main chain composed of fluorocarbon group vinyl monomer and hydrocarbon group vinyl monomer, and side chains having a primary molecular structure expressed.



(pは1～4のいずれかの整数)

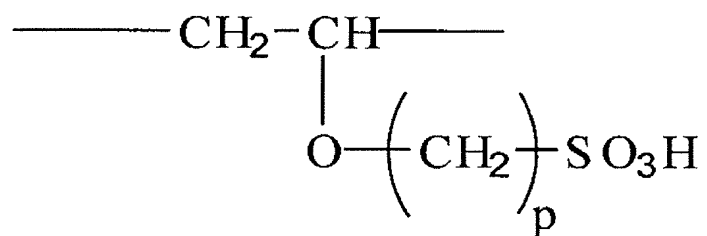
CLAIMS

[Claim(s)]

[Claim 1]

A main chain formed with a copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer,

[Chemical formula 1]



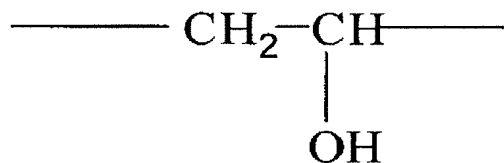
(p は 1 ～ 4 のいずれかの整数)

Solid polyelectrolyte membrane, wherein a side chain which has the 1st molecular structure expressed with ***** is formed.

[Claim 2]

Said side chain.

[Chemical formula 2]



The solid polyelectrolyte membrane according to claim 1 having the 2nd molecular structure expressed with *****.

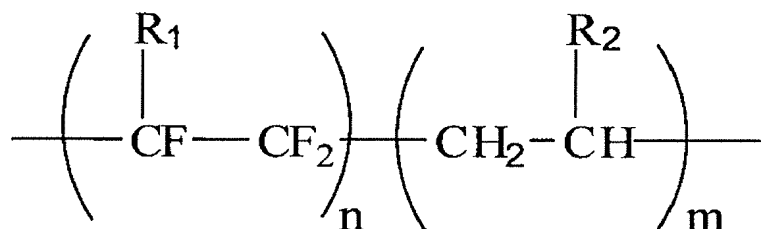
[Claim 3]

The solid polyelectrolyte membrane according to claim 2, wherein a weight ratio of said side chain to said main chain is larger than 0.5 and a mole ratio of said 1st molecular structure to the sum total of said 1st molecular structure and said 2nd molecular structure is larger than 0.2.

[Claim 4]

A copolymer of said carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer.

[Chemical formula 3]



(R 1 : フッ素原子または炭素数 1 ～ 3 のフルオロアルキル基、R 2 : 水素原子または炭素数 1 ～ 3 のアルキル基、m、n : 正の整数)

The solid polyelectrolyte membrane according to claim 1 which comes out and is characterized by a certain thing.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to solid polyelectrolyte membrane.

[0002]

[Description of the Prior Art]

The perfluorocarbon polymer films (trade name: Nafion, ASHIPU REXX, etc.) which generally have a sulfonic group as polymer electrolyte membrane for fuel cells are used, and good power generation performance and endurance are checked. However, for utilization, reduction and the

electrolyte membrane which made hydrogen ion conductivity high further of cost are expected. There is a hydrocarbon system electrolyte membrane to correspond to this.

[0003]

The solid polymer electrolyte of the hydrocarbon system which reformed the ethylene-vinylacetate copolymer to JP,H6-206938,A, and introduced the sulfonic group into it as conventional technology is indicated.

[0004]

[Problem to be solved by the invention]

However, in conventional technology, an ethylene-vinylacetate copolymer is reformed and the film is produced with an introductory post heating press in the sulfonic group. For this reason, it is soft depending on an ethylene-vinylacetate copolymer, and since film strength does not have addition of a cross linking agent, the dimensional change at the time of membranous water is also remarkable [film strength]. In order to produce a film with heat pressing, degradation of polymer is caused, and it becomes a cause of a fall of a film property. Therefore, as for the made film, the rate of a dimensional change turns into large desiccation in a fuel cell, and solid polyelectrolyte membrane with insufficient film durability in humid conditions.

[0005]

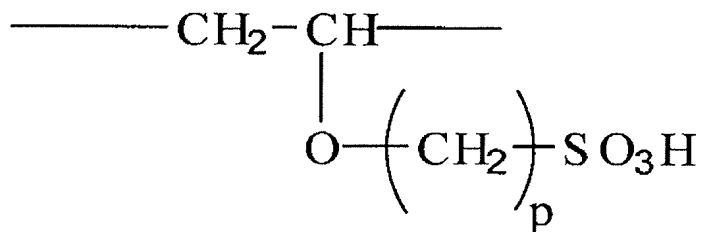
This invention provides the solid polyelectrolyte membrane which is what solved the aforementioned problem, and is low cost, and was excellent in endurance.

[0006]

[Means for solving problem]

The main chain in which the technical means (the 1st technical means are called hereafter.) provided in Claim 1 of this invention were formed with the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer in order to solve above-mentioned technical problem,

[Chemical formula 1]



(p は 1 ～ 4 のいずれかの整数)

It is solid polyelectrolyte membrane, wherein the side chain which has the 1st molecular structure expressed with ***** is formed.

[0007]

The effect by the 1st technical means of the above is as follows.

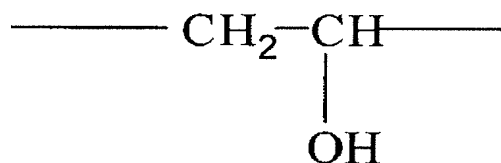
[0008]

That is, with pliability with a moderate copolymer of the carbonization fluorine system vinyl monomer and hydrocarbon system vinyl monomer which were used as a main chain, since there are few dimensional changes, desiccation and solid polyelectrolyte membrane excellent in the endurance in humid conditions are made. Since both the fluorinated part and the part which is not fluorinated exist, the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, When a main chain cutting-die radical and an intermolecular cross linkage type radical generate simultaneously, membranous intensity can be maintained making a radical generate moderately, and solid polyelectrolyte membrane excellent in endurance is made. Since the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer was furthermore used as a main chain, -izing can be carried out [low cost] as compared with a perfluorocarbon polymer film.

[0009]

In order to solve above-mentioned technical problem, said side chain the technical means (the 2nd technical means are called hereafter.) provided in Claim 2 of this invention,

[Chemical formula 2]



It is the solid polyelectrolyte membrane according to claim 1 having the 2nd molecular structure expressed with *****.

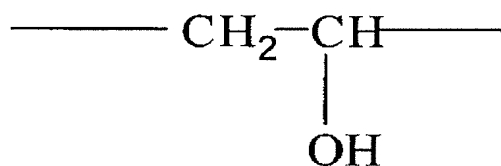
[0010]

The effect by the 2nd technical means of the above is as follows.

[0011]

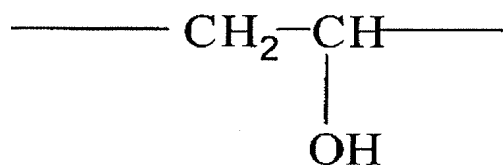
namely

[Chemical formula 2]



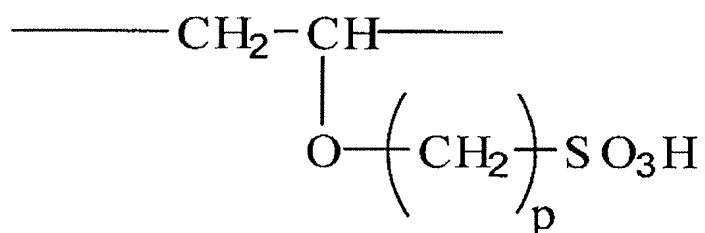
Since it is the structure of having ***** , water can be held by a hydrogen bond and the effect used as the solid polyelectrolyte membrane excellent in water retention is done so. moreover

[Chemical formula 2]



★★

[Chemical formula 1]



(p は 1 ～ 4 のいずれかの整数)

Since it is the structure boiled and changed, the effect of becoming easy to manufacture the 1st molecular structure is done so by having the 2nd molecular structure.

[0012]

In order to solve above-mentioned technical problem, the technical means (the 3rd technical means are called hereafter.) provided in Claim 3 of this invention, It is the solid polyelectrolyte membrane according to claim 2, wherein the weight ratio of said side chain to said main chain is larger than 0.5 and the mole ratio of said 1st molecular structure to the sum total of said 1st molecular structure and said 2nd molecular structure is larger than 0.2.

[0013]

The effect by the 3rd technical means of the above is as follows.

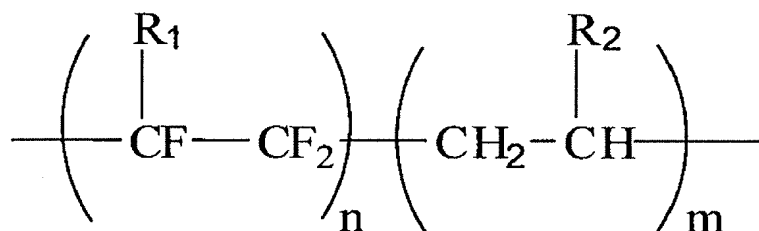
[0014]

Namely, solid polyelectrolyte membrane which was excellent in ion conductivity since the weight ratio to the main chain of the side chain which has hydrogen ion conductivity was larger than 0.5 is made, And since the 1st molecular structure mole ratio to the sum total of the 1st molecular structure and the 2nd molecular structure is larger than 0.2 and solid polyelectrolyte membrane excellent in endurance is made, solid polyelectrolyte membrane which was excellent in ion conductivity and was excellent in endurance is made.

[0015]

In order to solve above-mentioned technical problem, the copolymer of said carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer the technical means (the 4th technical means are called hereafter.) provided in Claim 4 of this invention,

[Chemical formula 3]



(R 1 : フッ素原子または炭素数 1 ~ 3 のフルオロアルキル基、R 2 : 水素原子または炭素数 1 ~ 3 のアルキル基、m、n : 正の整数)

It is the solid polyelectrolyte membrane according to claim 1 which comes out and is characterized by a certain thing.

[0016]

An effect by the 4th technical means of the above is as follows.

[0017]

That is, with a carbonization fluorine system vinyl polymerization object, if a radiation graft is performed, generation of a main chain cutting-die radical will be remarkable, and graft polymerization will be impossible, but

an effect whose radiation graft polymerization becomes possible is done so by using a copolymer with a hydrocarbon system vinyl monomer.

[0018]

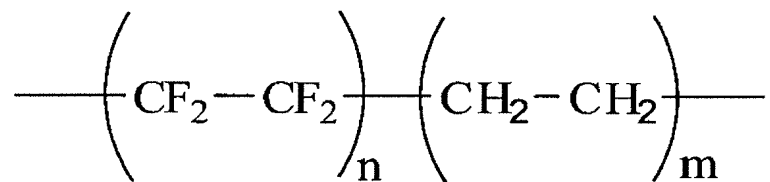
[Mode for carrying out the invention]

Hereafter, this invention is explained in detail. In order to explain simply, it explains using an ethylene tetrafluoroethylene copolymer as a copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer. An ethylene tetrafluoroethylene copolymer is expressed with a chemical formula (1).

[0019]

[Chemical formula 4]

化学式 (1)



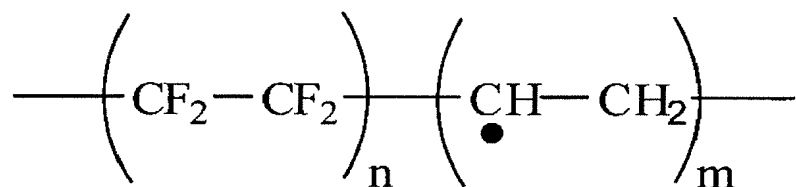
(m、n は正の整数)

When this ethylene tetrafluoroethylene copolymer was irradiated with radiation under a vacuum or an inert gas atmosphere, a radical generated to a part of ethylene, and it was expressed with a chemical formula (2).

[0020]

[Chemical formula 5]

化学式（2）



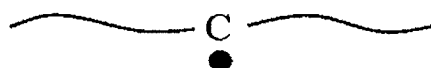
（m、n は正の整数）

The following explanation expresses said chemical formula (2) with a chemical formula (3).

[0021]

[Chemical formula 6]

化学式（3）

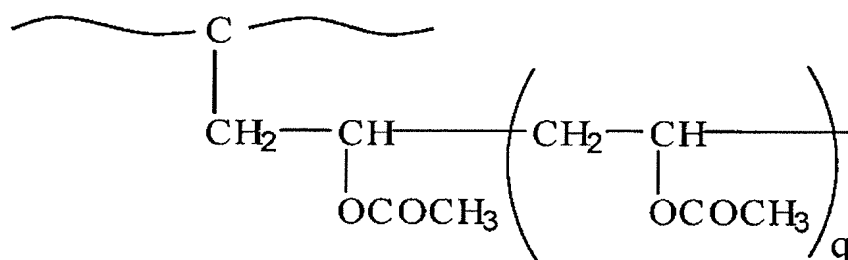


A film which polymerizes vinyl acetate in a chemical formula (3), carries out a graft to it, and is expressed with a chemical formula (4) was obtained.

[0022]

[Chemical formula 7]

化学式 (4)



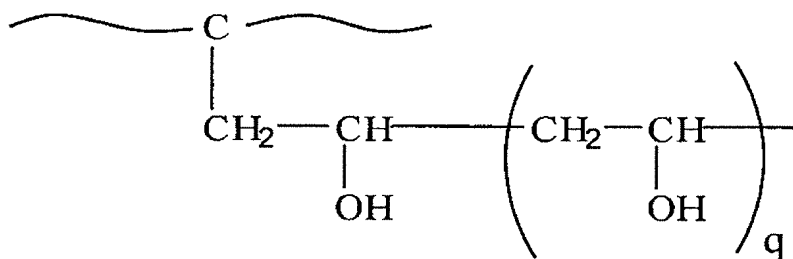
(q は正の整数)

If hydrolysis treatment is carried out to this film, it will become a film shown in a chemical formula (5).

[0023]

[Chemical formula 8]

化学式 (5)



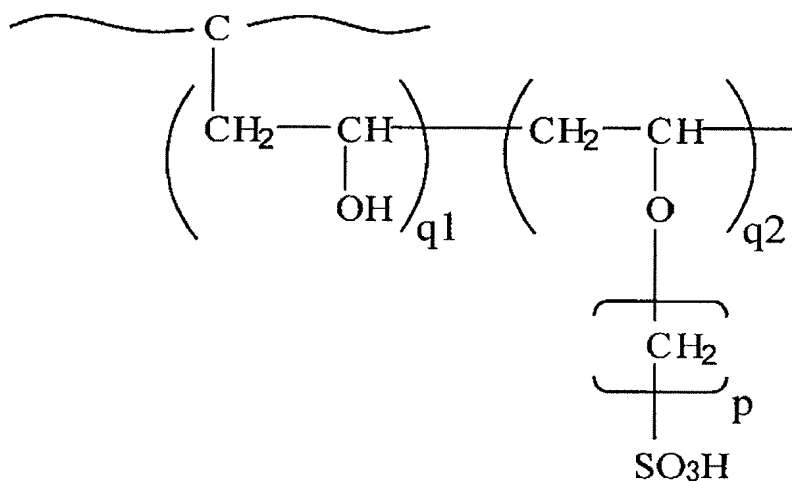
(q は正の整数)

By carrying out alkyl sulfonation treatment to the last, solid polyelectrolyte membrane shown in a chemical formula (6) was obtained.

[0024]

[Chemical formula 9]

化学式 (6)



(q 1、2は正の整数、 p は 1 ～ 4 のいずれかの整数)

Since this film has a main chain of the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, with moderate pliability, there are few dimensional changes and it can do desiccation and solid polyelectrolyte membrane excellent in the endurance in humid conditions. Since both the fluorinated part and the part which is not fluorinated exist, the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, When a main chain cutting-die radical and an intermolecular cross linkage type radical generate simultaneously, membranous intensity can be maintained making a radical generate moderately, and solid polyelectrolyte membrane excellent in endurance is made. Since the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer was furthermore used as a main chain,-izing can be carried out [low cost] as compared with a perfluorocarbon polymer film.

[0025]

In the solid polyelectrolyte membrane shown in the chemical formula (7)

which formed in the main chain of the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer the graft styrene side chain which has a benzene group, and was produced. The hydrogen combined with the carbon combined with the benzene group was extracted by the active oxygen generated at the time of the electrode reaction of a fuel cell, this carbon became radical, the autoxidation of the electrolyte membrane arose and there was a deteriorating problem. On the other hand, in the solid polyelectrolyte membrane of this invention, since a benzene group does not exist, autoxidation is not produced. Therefore, the solid polyelectrolyte membrane of this invention is excellent in endurance also from this point.

[0026]

Hereafter, the embodiment of this invention is described. In the following embodiments, the film of the ethylene tetrafluoroethylene copolymer which is a copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer is used as a raw material of solid polyelectrolyte membrane. The thickness of this film is 50 micrometers. This ethylene tetrafluoroethylene copolymer serves as a main chain formed with the copolymer of the carbonization fluorine system vinyl monomer of solid polyelectrolyte membrane and hydrocarbon system vinyl monomer which were manufactured.

[0027]

(EXAMPLE)

After acetone washed the film of the ethylene tetrafluoroethylene copolymer, it irradiated with the gamma ray of 20K Gy, using ⁶⁰Co as a radiation source. After putting obtained film 10cm² into a glass coil, 70 g of vinyl acetate monomers were added to the coil, and nitrogen fully replaced the inside of a coil (graft processing).

[0028]

Then, this coil was immersed in a 70 °C thermostat for 8 hours. After methanol washed the film after a reaction 3 times, it was made to dry using a dryer. After making the solution of two copies (a weight section and the following -- the same) of sodium hydroxide, and 98 copies of methanol immerse 55 °C of ester exchange reactions of a dry film for 3 hours, methanol washed them (hydrolysis treatment). It was checked that ion exchange water furthermore washed the film, it was made to dry at 100 °C

for 3 hours, and the acetyl group had been replaced by the hydroxyl group about 100% from the amount of weight changes, and IR (infrared-absorption analysis) data.

[0029]

After the sulfonic group introduction reaction of the obtained film put the film into the glass coil, it put in distilled dimethyl sulfoxide $3 \times 10^{-5} \text{m}^3$, and fully replaced the inside of a coil with nitrogen. 0.5g of sodium hydride was put in it, and it warmed at 60 **, and was made to react for 1 hour. It dissolved in dimethyl sulfoxide 10^{-5}m^3 which distilled propane Salton 2g to reaction mixture, this was dropped over 1 hour, and it was made to react at 80 ** after that for 7 hours (alkyl sulfonation treatment). Took out the after-reaction film, this was made immersed in the solution of hydrochloric acid of 1N at 50 ** for 8 hours, ion exchange water fully washed, and solid polyelectrolyte membrane was obtained.

[0030]

Although propane Salton is used as a sulfonating agent here, 2-bromoethane sulfone sodium, a 1,4-butanedisulfone, etc. can be used.

[0031]

The intensity evaluation of the obtained solid polyelectrolyte membrane carries out the water of the solid polyelectrolyte membrane to 90 ** hot water enough, Start the solid polyelectrolyte membrane (95 micrometers of thickness) which carried out water to 30 mm x 30 mm, and it puts on the middle of the fixture of drawing 1, It put and fixed with the fixture of another drawing 1, this was respectively put in alternately for 1 hour under [of 90 **] the dry heat condition and the 95% of 90 ** humidity condition, and the number of cycles until it fractures by membranous elasticity was measured.

[0032]

(Comparative example)

A comparative example is the solid polyelectrolyte membrane of the hydrocarbon system which reformed the ethylene-vinylacetate copolymer of conventional technology and introduced the sulfonic group. Manufacture of this solid polyelectrolyte membrane was performed by the method shown below.

[0033]

25 g of ethylene-vinylacetate copolymers (about 40% of vinyl acetate

content) are dissolved in toluene 10^{-4}m^3 , In this, methanol $5 \times 10^{-5}\text{m}^3$ and 5 g of sodium hydroxide were put, it was made to react for 2 hours, 65 ** of methanol $5 \times 10^{-4}\text{m}^3$ was added after that, the ** exception carried out the sediment, and polymer was collected. This polymer was enough dried with an 85 ** vacuum dryer. It dissolved in tetrahydrofuran $5 \times 10^{-5}\text{m}^3$ which distilled 7 g of polymer dried enough, the sodium hydride 1.8g and distilled dimethyl sulfoxide $5 \times 10^{-5}\text{m}^3$ were put in this, and it warmed at 60 **, and was made to react for 2 hours. Reaction mixture was 80 ** dropping and after that over 1 hour, and propane Salton 10g dissolved in tetrahydrofuran $2 \times 10^{-5}\text{m}^3$ distilled to this reaction mixture was made to react for 8 hours. Reaction mixture was put into acetone of 10^{-3}m^3 , the ** exception carried out the sediment, and polymer was collected. Ion exchange water often washed the collected polymer, and after putting into 1N chloride 10^{-3}m^3 and being immersed for 12 hours, ion exchange water washed well further. Dry polymer was inserted into the aluminum board of 2g picking and 1-mm thickness, it pressed for 2 minutes by 130 ** and 4.9MPa, and the film was produced. The water of this film was enough carried out to 90 ** hot water, and the solid polyelectrolyte membrane of 100-micrometer thickness was obtained. The intensity evaluation of the obtained solid polyelectrolyte membrane did the same examination as an embodiment.

[0034]

(Intensity evaluation result)

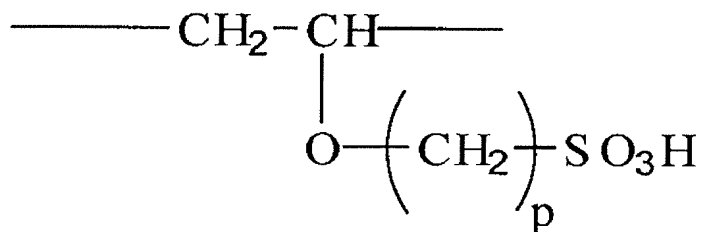
As for the solid polyelectrolyte membrane of the embodiment, change was not seen although the solid polyelectrolyte membrane of the comparative example was fractured from the center of a film after 100 cycle *****. As for the membranous fracture, 400 cycle ***** was not seen after that.

[0035]

[Effect of the Invention]

As mentioned above, the main chain with which this invention was formed with the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer,

[Chemical formula 1]



(p は 1 ~ 4 のいずれかの整数)

Since it is solid polyelectrolyte membrane, wherein the side chain which has the 1st molecular structure expressed with ***** is formed, the solid polyelectrolyte membrane excellent in endurance can be provided by low cost.

[Brief Description of the Drawings]

[Drawing 1] The perspective view of a fixture

[Explanations of letters or numerals]

1 -- Intensity measurement fixture

2 -- Through hole part

TECHNICAL FIELD

[Field of the Invention]

This invention relates to solid polyelectrolyte membrane.

[0002]

PRIOR ART

[Description of the Prior Art]

The perfluorocarbon polymer films (trade name: Nafion, ASHIPU REXX, etc.) which generally have a sulfonic group as polymer electrolyte membrane for fuel cells are used, and good power generation performance and endurance are checked. However, for utilization, reduction and the

electrolyte membrane which made hydrogen ion conductivity high further of cost are expected. There is a hydrocarbon system electrolyte membrane to correspond to this.

[0003]

The solid polymer electrolyte of the hydrocarbon system which reformed the ethylene-vinylacetate copolymer to JP,H6-206938,A, and introduced the sulfonic group into it as conventional technology is indicated.

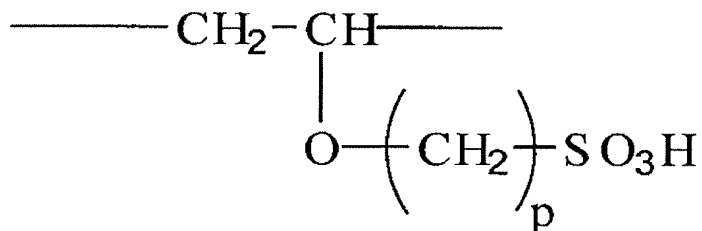
[0004]

EFFECT OF THE INVENTION

[Effect of the Invention]

As mentioned above, the main chain with which this invention was formed with the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer,

[Chemical formula 1]



(p は 1 ~ 4 のいずれかの整数)

Since it is solid polyelectrolyte membrane, wherein the side chain which has the 1st molecular structure expressed with ***** is formed, the solid polyelectrolyte membrane excellent in endurance can be provided by low cost.

TECHNICAL PROBLEM

[Problem to be solved by the invention]

However, in conventional technology, an ethylene–vinylacetate copolymer is reformed and the film is produced with an introductory post heating press in the sulfonic group. For this reason, it is soft depending on an ethylene–vinylacetate copolymer, and since film strength does not have addition of a cross linking agent, the dimensional change at the time of membranous water is also remarkable [film strength]. In order to produce a film with heat pressing, degradation of polymer is caused, and it becomes a cause of a fall of a film property. Therefore, as for the made film, the rate of a dimensional change turns into large desiccation in a fuel cell, and solid polyelectrolyte membrane with insufficient film durability in humid conditions.

[0005]

This invention provides the solid polyelectrolyte membrane which is what solved the aforementioned problem, and is low cost, and was excellent in endurance.

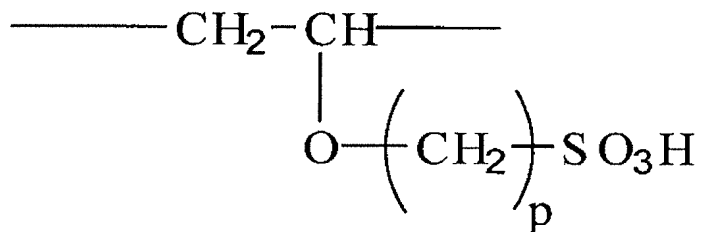
[0006]

MEANS

[Means for solving problem]

The main chain in which the technical means (the 1st technical means are called hereafter.) provided in Claim 1 of this invention were formed with the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer in order to solve above–mentioned technical problem,

[Chemical formula 1]



(p は 1 ～ 4 のいずれかの整数)

It is solid polyelectrolyte membrane, wherein the side chain which has the 1st molecular structure expressed with ***** is formed.

[0007]

The effect by the 1st technical means of the above is as follows.

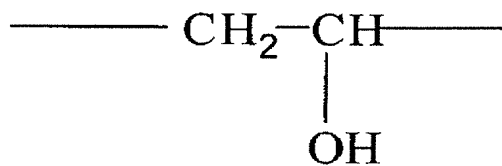
[0008]

That is, with pliability with a moderate copolymer of the carbonization fluorine system vinyl monomer and hydrocarbon system vinyl monomer which were used as a main chain, since there are few dimensional changes, desiccation and solid polyelectrolyte membrane excellent in the endurance in humid conditions are made. Since both the fluorinated part and the part which is not fluorinated exist, the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, When a main chain cutting-die radical and an intermolecular cross linkage type radical generate simultaneously, membranous intensity can be maintained making a radical generate moderately, and solid polyelectrolyte membrane excellent in endurance is made. Since the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer was furthermore used as a main chain, -izing can be carried out [low cost] as compared with a perfluorocarbon polymer film.

[0009]

In order to solve above-mentioned technical problem, said side chain the technical means (the 2nd technical means are called hereafter.) provided in Claim 2 of this invention,

[Chemical formula 2]



It is the solid polyelectrolyte membrane according to claim 1 having the 2nd molecular structure expressed with *****.

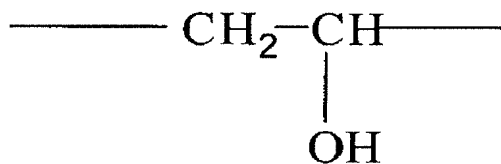
[0010]

The effect by the 2nd technical means of the above is as follows.

[0011]

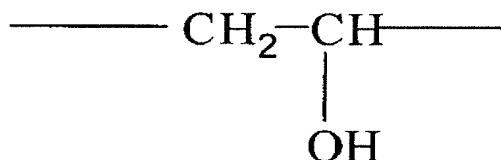
namely

[Chemical formula 2]



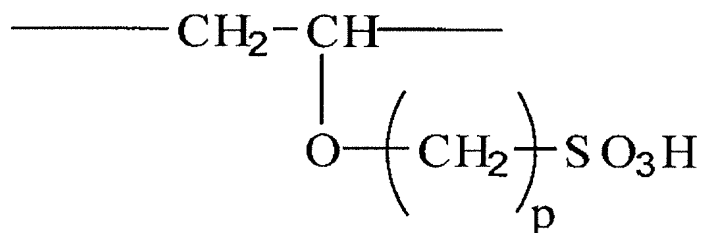
Since it is the structure of having *****, water can be held by a hydrogen bond and the effect used as the solid polyelectrolyte membrane excellent in water retention is done so. moreover

[Chemical formula 2]



**

[Chemical formula 1]



(p は 1 ～ 4 のいずれかの整数)

Since it is the structure boiled and changed, an effect of becoming easy to manufacture the 1st molecular structure is done so by having the 2nd molecular structure.

[0012]

In order to solve above-mentioned technical problem, technical means (the 3rd technical means are called hereafter.) provided in Claim 3 of this invention, It is the solid polyelectrolyte membrane according to claim 2, wherein a weight ratio of said side chain to said main chain is larger than 0.5 and a mole ratio of said 1st molecular structure to the sum total of said 1st molecular structure and said 2nd molecular structure is larger than 0.2.

[0013]

An effect by the 3rd technical means of the above is as follows.

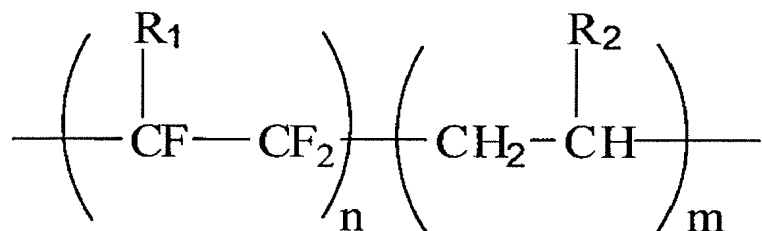
[0014]

Namely, solid polyelectrolyte membrane which was excellent in ion conductivity since the weight ratio to a main chain of a side chain which has hydrogen ion conductivity was larger than 0.5 is made, And since the 1st molecular structure mole ratio to the sum total of the 1st molecular structure and the 2nd molecular structure is larger than 0.2 and solid polyelectrolyte membrane excellent in endurance is made, solid polyelectrolyte membrane which was excellent in ion conductivity and was excellent in endurance is made.

[0015]

In order to solve above-mentioned technical problem, a copolymer of said carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer technical means (the 4th technical means are called hereafter.) provided in Claim 4 of this invention,

[Chemical formula 3]



(R 1 : フッ素原子または炭素数 1 ~ 3 のフルオロアルキル基、R 2 : 水素原子または炭素数 1 ~ 3 のアルキル基、m、n : 正の整数)

It is the solid polyelectrolyte membrane according to claim 1 which comes out and is characterized by a certain thing.

[0016]

The effect by the 4th technical means of the above is as follows.

[0017]

That is, with a carbonization fluorine system vinyl polymerization object, if a radiation graft is performed, generation of a main chain cutting-die radical will be remarkable, and graft polymerization will be impossible, but the effect whose radiation graft polymerization becomes possible is done

so by using a copolymer with a hydrocarbon system vinyl monomer.

[0018]

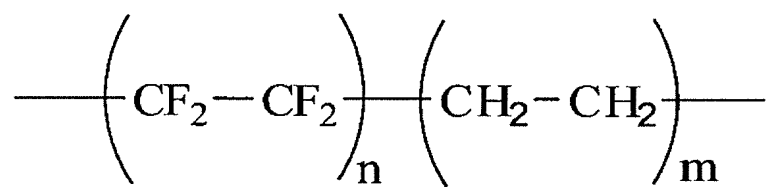
[Mode for carrying out the invention]

Hereafter, this invention is explained in detail. In order to explain simply, it explains using an ethylene tetrafluoroethylene copolymer as a copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer. An ethylene tetrafluoroethylene copolymer is expressed with a chemical formula (1).

[0019]

[Chemical formula 4]

化学式（１）



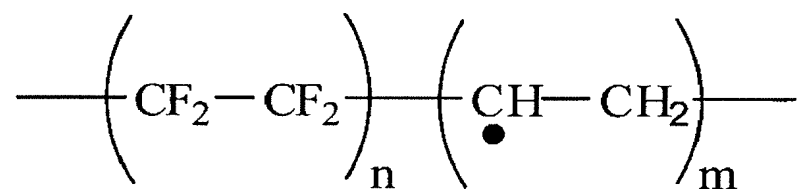
（m、nは正の整数）

When this ethylene tetrafluoroethylene copolymer was irradiated with radiation under a vacuum or an inert gas atmosphere, the radical generated to a part of ethylene, and it was expressed with the chemical formula (2).

[0020]

[Chemical formula 5]

化学式 (2)



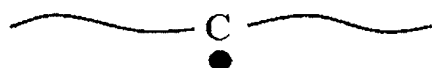
(m、n は正の整数)

The following explanation expresses said chemical formula (2) with a chemical formula (3).

[0021]

[Chemical formula 6]

化学式 (3)

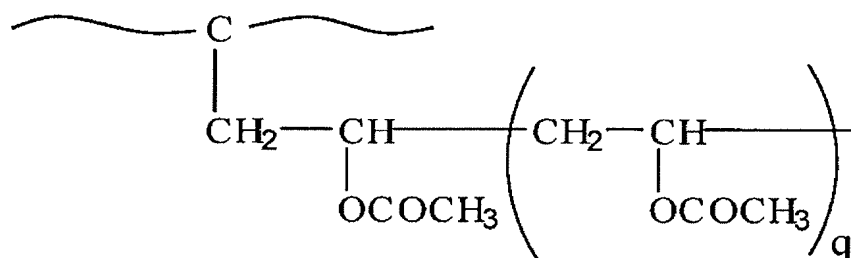


The film which polymerizes vinyl acetate in a chemical formula (3), carries out a graft to it, and is expressed with a chemical formula (4) was obtained.

[0022]

[Chemical formula 7]

化学式 (4)



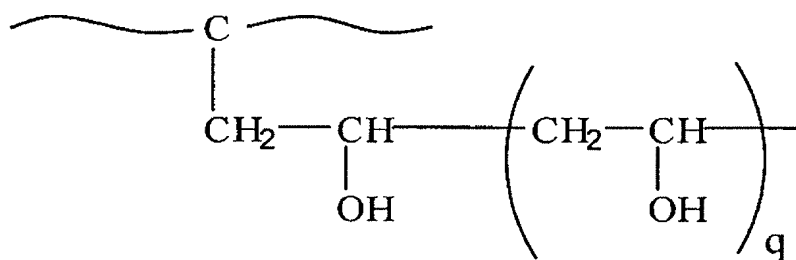
(q は正の整数)

If hydrolysis treatment is carried out to this film, it will become a film shown in a chemical formula (5).

[0023]

[Chemical formula 8]

化学式 (5)



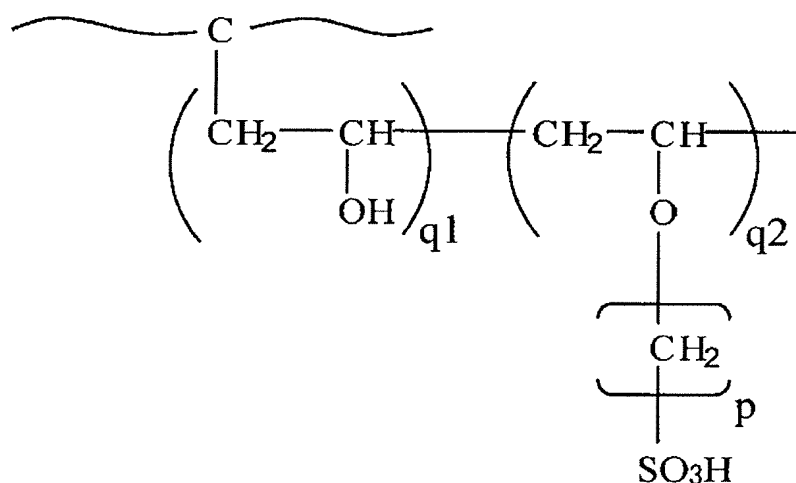
(q は正の整数)

By carrying out alkyl sulfonation treatment to the last, the solid polyelectrolyte membrane shown in the chemical formula (6) was obtained.

[0024]

[Chemical formula 9]

化学式 (6)



(q_1 、 q_2 は正の整数、 p は1～4のいずれかの整数)

Since this film has a main chain of the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, with moderate pliability, there are few dimensional changes and it can do desiccation and solid polyelectrolyte membrane excellent in the endurance in humid conditions. Since both the fluorinated part and the part which is not fluorinated exist, the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer, When a main chain cutting-die radical and an intermolecular cross linkage type radical generate simultaneously, membranous intensity can be maintained making a radical generate moderately, and solid polyelectrolyte membrane excellent in endurance is made. Since the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer was furthermore used as a main chain,-izing can be carried out [low cost] as compared with a perfluorocarbon polymer film.

[0025]

In the solid polyelectrolyte membrane shown in the chemical formula (7)

which formed in the main chain of the copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer the graft styrene side chain which has a benzene group, and was produced. The hydrogen combined with the carbon combined with the benzene group was extracted by the active oxygen generated at the time of the electrode reaction of a fuel cell, this carbon became radical, the autoxidation of the electrolyte membrane arose and there was a deteriorating problem. On the other hand, in the solid polyelectrolyte membrane of this invention, since a benzene group does not exist, autoxidation is not produced. Therefore, the solid polyelectrolyte membrane of this invention is excellent in endurance also from this point.

[0026]

Hereafter, an embodiment of this invention is described. In the following embodiments, a film of an ethylene tetrafluoroethylene copolymer which is a copolymer of a carbonization fluorine system vinyl monomer and a hydrocarbon system vinyl monomer is used as a raw material of solid polyelectrolyte membrane. Thickness of this film is 50 micrometers. This ethylene tetrafluoroethylene copolymer serves as a main chain formed with a copolymer of a carbonization fluorine system vinyl monomer of solid polyelectrolyte membrane and a hydrocarbon system vinyl monomer which were manufactured.

[0027]

EXAMPLE

(EXAMPLE)

After acetone washed the film of the ethylene tetrafluoroethylene copolymer, it irradiated with the gamma ray of 20KGy; using ^{60}Co as a radiation source. After putting obtained film 10cm^2 into a glass coil, 70 g of vinyl acetate monomers were added to the coil, and nitrogen fully replaced the inside of a coil (graft processing).

[0028]

Then, this coil was immersed in a 70 °C thermostat for 8 hours. After methanol washed the film after a reaction 3 times, it was made to dry using a dryer. after making the solution of two copies (a weight section and the

following -- the same) of sodium hydroxide, and 98 copies of methanol immerse 55 ** of ester exchange reactions of a dry film for 3 hours, methanol washed them (hydrolysis treatment). It was checked that ion exchange water furthermore washed the film, it was made to dry at 100 ** for 3 hours, and the acetyl group had been replaced by the hydroxyl group about 100% from the amount of weight changes, and IR (infrared-absorption analysis) data.

[0029]

After the sulfonic group introduction reaction of the obtained film put the film into the glass coil, it put in distilled dimethyl sulfoxide $3 \times 10^{-5} \text{m}^3$, and fully replaced the inside of a coil with nitrogen. 0.5g of sodium hydride was put in it, and it warmed at 60 **, and was made to react for 1 hour. It dissolved in dimethyl sulfoxide 10^{-5}m^3 which distilled propane Salton 2g to reaction mixture, this was dropped over 1 hour, and it was made to react at 80 ** after that for 7 hours (alkyl sulfonation treatment). Took out the after-reaction film, this was made immersed in the solution of hydrochloric acid of 1N at 50 ** for 8 hours, ion exchange water fully washed, and solid polyelectrolyte membrane was obtained.

[0030]

Although propane Salton is used as a sulfonating agent here, 2-bromoethane sulfone sodium, a 1,4-butanedisulfone, etc. can be used.

[0031]

The intensity evaluation of the obtained solid polyelectrolyte membrane carries out the water of the solid polyelectrolyte membrane to 90 ** hot water enough, Start the solid polyelectrolyte membrane (95 micrometers of thickness) which carried out water to 30 mm x 30 mm, and it puts on the middle of the fixture of drawing 1, It put and fixed with the fixture of another drawing 1, this was respectively put in alternately for 1 hour under [of 90 **] the dry heat condition and the 95% of 90 ** humidity condition, and the number of cycles until it fractures by membranous elasticity was measured.

[0032]

(Comparative example)

A comparative example is the solid polyelectrolyte membrane of the hydrocarbon system which reformed the ethylene-vinylacetate copolymer of conventional technology and introduced the sulfonic group. Manufacture

of this solid polyelectrolyte membrane was performed by the method shown below.

[0033]

25 g of ethylene-vinylacetate copolymers (about 40% of vinyl acetate content) are dissolved in toluene 10^{-4}m^3 , In this, methanol $5 \times 10^{-5}\text{m}^3$ and 5 g of sodium hydroxide were put, it was made to react for 2 hours, 65 ** of methanol $5 \times 10^{-4}\text{m}^3$ was added after that, the ** exception carried out the sediment, and polymer was collected. This polymer was enough dried with an 85 ** vacuum dryer. It dissolved in tetrahydrofuran $5 \times 10^{-5}\text{m}^3$ which distilled 7 g of polymer dried enough, the sodium hydride 1.8g and distilled dimethyl sulfoxide $5 \times 10^{-5}\text{m}^3$ were put in this, and it warmed at 60 **, and was made to react for 2 hours. Reaction mixture was 80 ** dropping and after that over 1 hour, and propane Salton 10g dissolved in tetrahydrofuran $2 \times 10^{-5}\text{m}^3$ distilled to this reaction mixture was made to react for 8 hours. Reaction mixture was put into acetone of 10^{-3}m^3 , the ** exception carried out the sediment, and polymer was collected. Ion exchange water often washed the collected polymer, and after putting into 1N chloride 10^{-3}m^3 and being immersed for 12 hours, ion exchange water washed well further. Dry polymer was inserted into the aluminum board of 2g picking and 1-mm thickness, it pressed for 2 minutes by 130 ** and 4.9MPa, and the film was produced. The water of this film was enough carried out to 90 ** hot water, and the solid polyelectrolyte membrane of 100-micrometer thickness was obtained. The intensity evaluation of the obtained solid polyelectrolyte membrane did the same examination as an embodiment.

[0034]

(Intensity evaluation result)

As for the solid polyelectrolyte membrane of the embodiment, change was not seen although the solid polyelectrolyte membrane of the comparative example was fractured from the center of a film after 100 cycle *****. As for the membranous fracture, 400 cycle ***** was not seen after that.

[0035]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The perspective view of a fixture

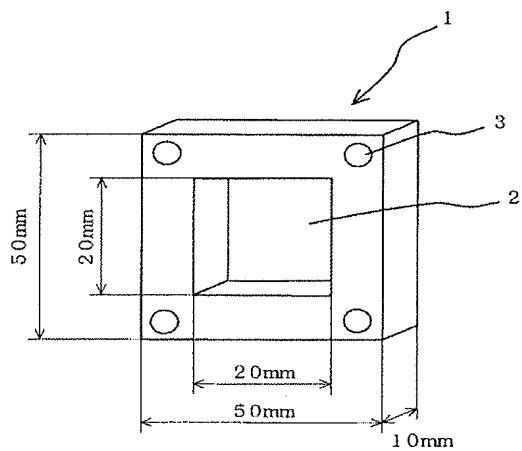
[Explanations of letters or numerals]

1 -- Intensity measurement fixture

2 -- Through hole part

DRAWINGS

[Drawing 1]



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 5H026 AA06 CX05 EE19

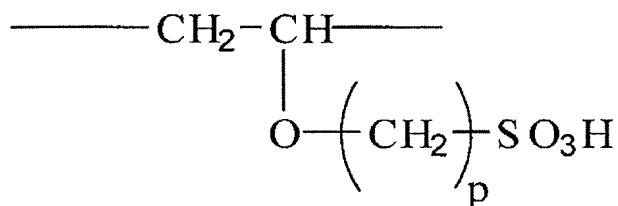
(54) 【発明の名称】 燃料電池用固体高分子電解質膜

(57) 【要約】

【課題】 低コストで、かつ耐久性に優れた固体高分子電解質膜を提供する。

【解決手段】 炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体で形成された主鎖と、

【化1】



(pは1～4のいずれかの整数)

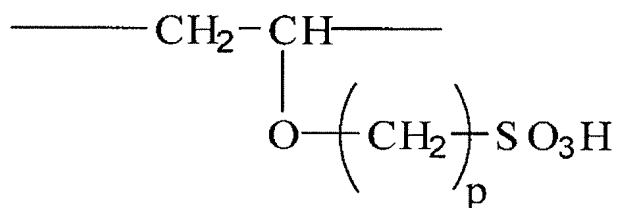
の化学式で表される第1分子構造を有する側鎖とが設けられていることを特徴とする固体高分子電解質膜。

【特許請求の範囲】

【請求項 1】

炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体で形成された主鎖と、

【化 1】



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(p は 1 ～ 4 のいずれかの整数)

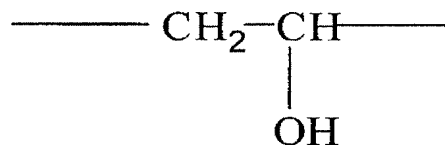
の化学式で表される第 1 分子構造を有する側鎖とが設けられていることを特徴とする固体高分子電解質膜。

【請求項 2】

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前記側鎖が

【化 2】



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の化学式で表される第 2 分子構造を有することを特徴とする請求項 1 記載の固体高分子電解質膜。

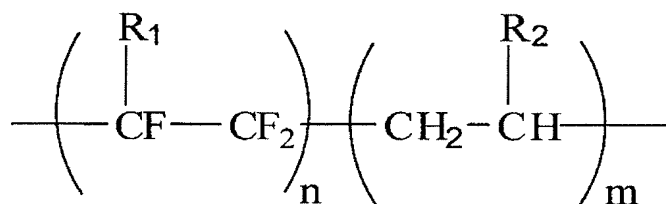
【請求項 3】

前記主鎖に対する前記側鎖の重量比が 0.5 より大きく、かつ前記第 1 分子構造と前記第 2 分子構造の合計に対する前記第 1 分子構造のモル比が 0.2 より大きいことを特徴とする請求項 2 記載の固体高分子電解質膜。

【請求項 4】

前記炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体が

【化 3】



(R 1 : フッ素原子または炭素数 1 ~ 3 のフルオロアルキル基、R 2 : 水素原子または炭素数 1 ~ 3 のアルキル基、m、n : 正の整数)

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であることを特徴とする請求項 1 記載の固体高分子電解質膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は固体高分子電解質膜に関する。

【0002】

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【従来の技術】

一般には燃料電池用高分子電解質膜としてスルホン酸基を有するパーフルオロカーボン重合体膜（商品名：ナフィオン、アシプレックス等）が用いられ、良好な発電性能と耐久性が確認されている。しかし、実用化のためにはコストの低減およびさらに水素イオン伝導性を高めた電解質膜が期待されている。これに該当するものとして炭化水素系電解質膜がある。

【0003】

従来技術として、特開平 6-206938 号公報には、エチレン-酢酸ビニル共重合体を改質しスルホン酸基を導入した炭化水素系の固体高分子電解質が開示されている。

【0004】

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【発明が解決しようとする課題】

しかしながら、従来技術では、エチレン-酢酸ビニル共重合体を改質しスルホン酸基を導入後熱プレスにより製膜をおこなっている。このため膜強度はエチレン-酢酸ビニル共重合体に依存し、柔らかく、架橋剤の添加がないため膜の含水時の寸法変化も著しい。また、熱プレスにより製膜を行うためポリマーの劣化を起し、膜物性の低下原因となる。よってできた膜は寸法変化率が大きく燃料電池における乾燥、湿潤条件での膜耐久性が不十分な固体高分子電解質膜となる。

【0005】

本発明は上記課題を解決したもので、低コストで、かつ耐久性に優れた固体高分子電解質膜を提供する。

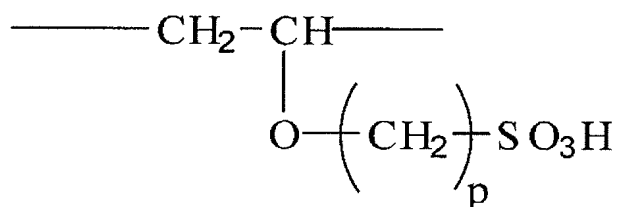
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【0006】

【課題を解決するための手段】

上記技術的課題を解決するために、本発明の請求項 1 において講じた技術的手段（以下、第 1 の技術的手段と称する。）は、炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体で形成された主鎖と、

【化 1】



(p は 1 ～ 4 のいずれかの整数)

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の化学式で表される第 1 分子構造を有する側鎖とが設けられていることを特徴とする固体高分子電解質膜である。

【0007】

上記第 1 の技術的手段による効果は、以下のものである。

【0008】

すなわち、主鎖として使用した炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体が適度な柔軟性を持ち寸法変化が少ないため、乾燥、湿潤条件での耐久性に優れた固体高分子電解質膜ができる。また炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体はフッ素化された部位とフッ素化されていない部位の両方が存在するので、主鎖切断型ラジカルと分子間架橋型ラジカルとが同時に生成することにより、適度にラジカルを生成させつつ膜の強度を保つことができ、耐久性に優れた固体高分子電解質膜ができる。さらに主鎖として炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体を使用したのも、パーフルオロカーボン重合体膜に比較して低コスト化

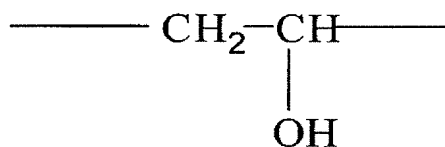
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【0009】

上記技術的課題を解決するために、本発明の請求項 2 において講じた技術的手段（以下、第 2 の技術的手段と称する。）は、前記側鎖が

【化 2】

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の化学式で表される第 2 分子構造を有することを特徴とする請求項 1 記載の固体高分子電解質膜である。

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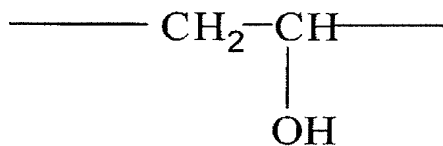
【0010】

上記第 2 の技術的手段による効果は、以下のものである。

【0011】

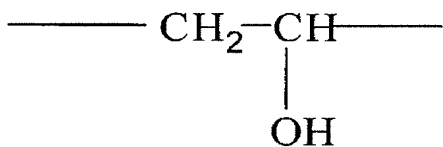
すなわち、

【化 2】



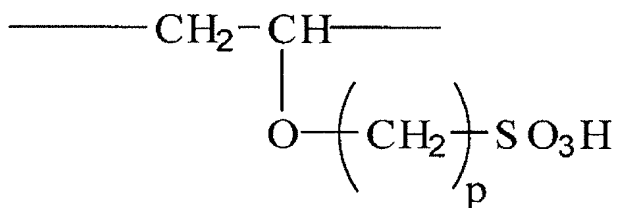
が水酸基を有する構造であるので、水素結合により水を保持することができ、保水性に優れた固体高分子電解質膜となる効果を奏する。また、

【化 2】



が

【化 1】



(p は 1 ～ 4 のいずれかの整数)

に変換される構造であるので、第 2 分子構造をもつことにより第 1 分子構造を製造しやすくなる効果を奏する。

【0012】

上記技術的課題を解決するために、本発明の請求項 3 において講じた技術的手段（以下、第 3 の技術的手段と称する。）は、前記主鎖に対する前記側鎖の重量比が 0.5 より大きく、かつ前記第 1 分子構造と前記第 2 分子構造の合計に対する前記第 1 分子構造のモル比が 0.2 より大きいことを特徴とする請求項 2 記載の固体高分子電解質膜である。

【0013】

上記第 3 の技術的手段による効果は、以下のようである。

【0014】

すなわち、水素イオン伝導性を有する側鎖の主鎖に対する重量比が 0.5 より大きいことによりイオン導電性に優れた固体高分子電解質膜ができ、かつ第 1 分子構造と第 2 分子構造の合計に対する第 1 分子構造モル比が 0.2 より大きいことにより耐久性に優れた固体高分子電解質膜ができるので、イオン導電性に優れ、かつ耐久性に優れた固体高分子電解質膜ができる。

【0015】

上記技術的課題を解決するために、本発明の請求項 4 において講じた技術的手段（以下、

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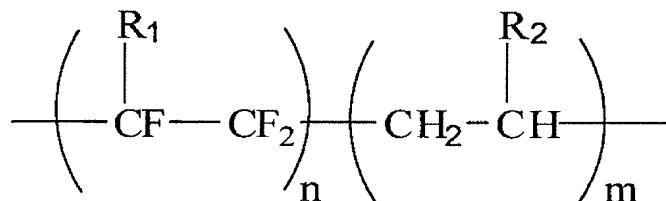
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第４の技術的手段と称する。)は、前記炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体が

【化３】



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(R 1 : フッ素原子または炭素数 1 ~ 3 のフルオロアルキル基、R 2 : 水素原子または炭素数 1 ~ 3 のアルキル基、m、n : 正の整数)

であることを特徴とする請求項 1 記載の固体高分子電解質膜である。

【００１６】

上記第４の技術的手段による効果は、以下のようなものである。

【００１７】

すなわち、炭化フッ素系ビニル重合体では放射線グラフトを行うと主鎖切断型ラジカルの生成が著しくグラフト重合ができないが、炭化水素系ビニルモノマーとの共重合体にするにより放射線グラフト重合が可能となる効果を奏する。

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【００１８】

【発明の実施の形態】

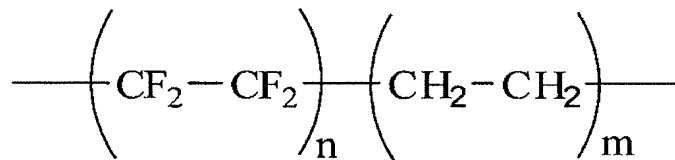
以下、本発明について詳しく説明する。説明を簡単にするため、炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体としてエチレンー四フッ化エチレン共重合体を用いて説明する。エチレンー四フッ化エチレン共重合体は化学式（１）で表される。

【００１９】

【化４】

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化学式（１）



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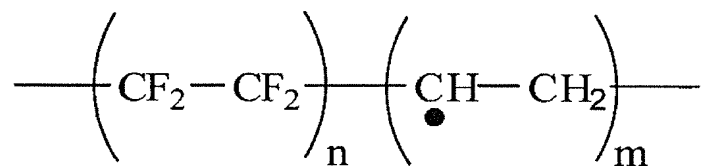
(m、n は正の整数)

このエチレンー四フッ化エチレン共重合体に真空または不活性ガス雰囲気下で放射線を照射するとエチレン基の一部にラジカルが生成し、それを化学式（２）で表した。

【００２０】

【化５】

化学式 (2)



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(m、n は正の整数)

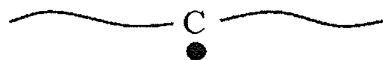
以下の説明では、前記化学式 (2) を化学式 (3) で表す。

【0021】

【化6】

化学式 (3)

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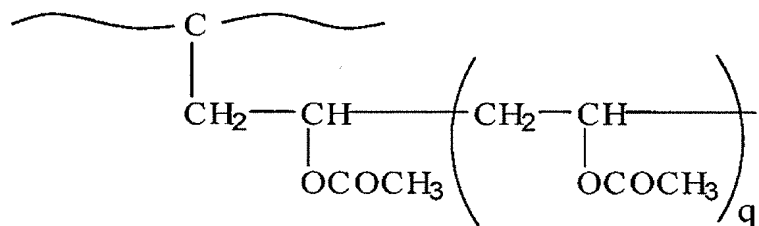
化学式 (3) に酢酸ビニルを重合させてグラフトし化学式 (4) で表されるフィルムを得た。

【0022】

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【化7】

化学式 (4)



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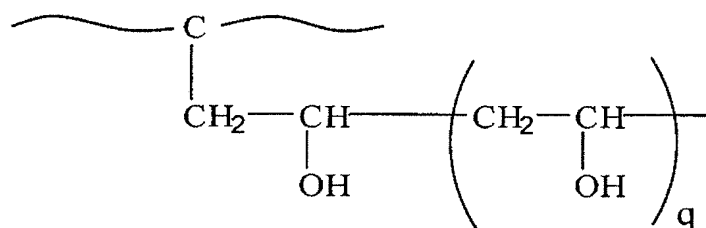
(q は正の整数)

このフィルムに加水分解処理をすると、化学式 (5) に示すフィルムとなる。

【0023】

【化8】

化学式 (5)



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(q は正の整数)

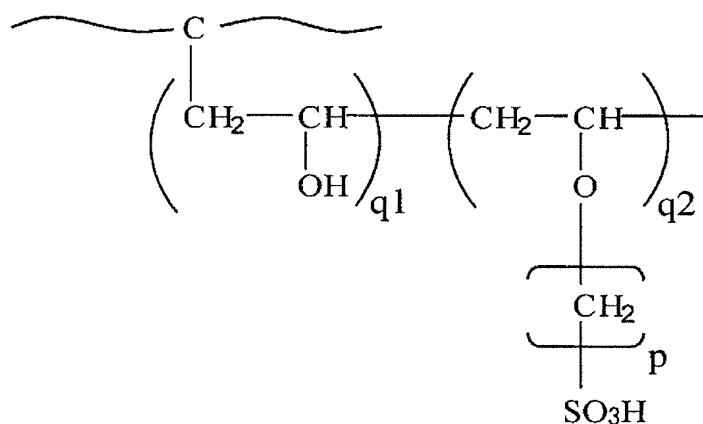
最後にアルキルスルホン化処理することで、化学式 (6) に示した固体高分子電解質膜を得た。

【0024】

【化9】

化学式 (6)

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(q1、2は正の整数、 p は1～4のいずれかの整数)

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この膜は、炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体の主鎖を持つため、適度な柔軟性を持ち寸法変化が少なく、乾燥、湿潤条件での耐久性に優れた固体高分子電解質膜ができる。また炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体はフッ素化された部位とフッ素化されていない部位の両方が存在するので、主鎖切断型ラジカルと分子間架橋型ラジカルとが同時に生成することにより、適度にラジカルを生成させつつ膜の強度を保つことができ、耐久性に優れた固体高分子電解質膜ができる。さらに主鎖として炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体を使用したので、パーフルオロカーボン重合体膜に比較して低コスト化できる。

【0025】

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炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体の主鎖にベンゼン基を有するグラフトスチレン側鎖を形成して作製された化学式(7)に示す固体高分子電解質膜では、ベンゼン基に結合した炭素に結合した水素が燃料電池の電極反応時に発生する活性酸素により抜かれ、この炭素がラジカルとなり、電解質膜の自動酸化が生じ、劣化する問題があった。これに対し、本発明の固体高分子電解質膜では、ベンゼン基は存在しないので、自動酸化は生じない。したがって、この点からも本発明の固体高分子電解質膜は耐久性に優れている。

【0026】

以下、本発明の実施例について説明する。以下の実施例では固体高分子電解質膜の原料として、炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体であるエチレンー四フッ化エチレン共重合体のフィルムを使用している。このフィルムの厚さは50 μm である。このエチレンー四フッ化エチレン共重合体が、製造された固体高分子電解質膜の炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体で形成された主鎖となる。

【0027】

(実施例)

エチレンー四フッ化エチレン共重合体のフィルムをアセトンで洗浄した後、放射線源としてコバルト60を用いて20 K G yのガンマ線を照射した。得られたフィルム10 cm^2 をガラス反応管に入れた後、酢酸ビニルモノマー70 gを反応管に加え、反応管の内部を十分に窒素で置換した(グラフト処理)。

【0028】

その後、かかる反応管を70℃の恒温槽に8時間浸漬した。反応後のフィルムをメタノールで3回洗浄した後、乾燥機を用いて乾燥させた。乾燥フィルムのエステル交換反応は、水酸化ナトリウム2部(重量部、以下同様)とメタノール98部の溶液に55℃3時間浸漬させた後、メタノールで洗浄した(加水分解処理)。さらにイオン交換水でフィルムを洗浄し、100℃で3時間乾燥させ重量変化量及びIR(赤外吸収分析)データよりアセチル基がほぼ100%水酸基に置換されたことを確認した。

【0029】

得られたフィルムのスルホン酸基導入反応は、ガラス反応管にフィルムを入れた後、蒸留したジメチルスルホキシド $3 \times 10^{-5} \text{ m}^3$ を入れ反応管の内部を十分に窒素で置換した。その中に水素化ナトリウムを0.5 g入れ60℃に加温し1時間反応させた。反応液にプロパンサルトン2 gを蒸留したジメチルスルホキシド 10^{-5} m^3 に溶解しこれを1時間かけて滴下し、その後80℃で7時間反応させた(アルキルスルホン化処理)。反応後フィルムを取り出し、これを1 Nの塩酸溶液に50℃で8時間浸漬させ、イオン交換水で十分に洗浄して固体高分子電解質膜を得た。

【0030】

なお、ここではスルホン化剤としてプロパンサルトンを使用しているが、2-ブロモエタンスルホン酸ナトリウム、1,4-ブタンサルトンなども使用できる。

【0031】

得られた固体高分子電解質膜の強度評価は、固体高分子電解質膜を90℃の熱水に十分含水させ、含水した固体高分子電解質膜(膜厚95 μm)を30 mm \times 30 mmに切り出し図1の治具の真ん中に置き、もう一つの図1の治具で挟み込んで固定し、これを90℃の乾熱条件下および90℃湿度95%条件下に各々1時間交互に入れ、膜の伸縮により破断するまでのサイクル数を測定した。

【0032】

(比較例)

比較例は、従来技術のエチレンー酢酸ビニル共重合体を改質しスルホン酸基を導入した炭化水素系の固体高分子電解質膜である。この固体高分子電解質膜の製造は下記に示す方法で行った。

【0033】

エチレン-酢酸ビニル共重合体（酢酸ビニル含量約40%）25gをトルエン 10^{-4} m^3 に溶解し、この中にメタノール $5 \times 10^{-5} \text{ m}^3$ と水酸化ナトリウム5gを入れ65℃、2時間反応させ、その後メタノール $5 \times 10^{-4} \text{ m}^3$ を加え沈殿物をろ別しポリマーを回収した。このポリマーを85℃の真空乾燥機で十分乾燥した。十分乾燥させたポリマー7gを蒸留したテトラヒドロフラン $5 \times 10^{-5} \text{ m}^3$ に溶解し、この中に水素化ナトリウム1.8gおよび蒸留したジメチルスルホキシド $5 \times 10^{-5} \text{ m}^3$ を入れ60℃に加温し2時間反応させた。この反応液に蒸留したテトラヒドロフラン $2 \times 10^{-5} \text{ m}^3$ に溶解したプロパンサルトン10gを1時間かけて滴下、その後反応液を80℃とし8時間反応させた。反応液を 10^{-3} m^3 のアセトンに入れ沈殿物をろ別しポリマーを回収した。回収したポリマーをよくイオン交換水で洗浄し、1N塩酸 10^{-3} m^3 に入れ12時間浸漬したのち、さらにイオン交換水で良く洗浄した。乾燥したポリマーを2g取り、1mm厚のアルミ板にはさみ、130℃、4.9MPaで2分間プレスしフィルムを作製した。このフィルムを90℃の熱水に十分含水させ100 μm 厚の固体高分子電解質膜を得た。得られた固体高分子電解質膜の強度評価は、実施例と同様な試験を行った。

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【0034】

（強度評価結果）

比較例の固体高分子電解質膜は100サイクル行った後、膜中央から破断していたが、実施例の固体高分子電解質膜は変化が見られなかった。その後400サイクル行ったが、膜の破断は見られなかった。

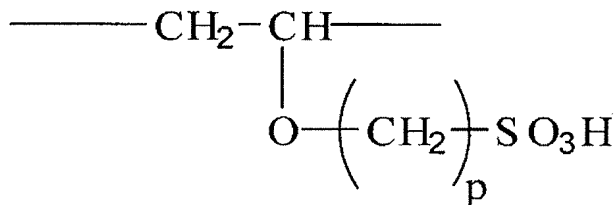
【0035】

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【発明の効果】

以上のように、本発明は、炭化フッ素系ビニルモノマーと炭化水素系ビニルモノマーとの共重合体で形成された主鎖と、

【化1】



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（pは1～4のいずれかの整数）

の化学式で表される第1分子構造を有する側鎖とが設けられていることを特徴とする固体高分子電解質膜であるので、耐久性に優れた固体高分子電解質膜を低コストで提供できる。

【図面の簡単な説明】

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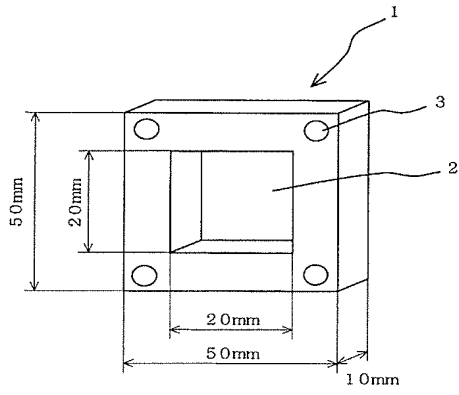
【図1】測定治具の斜視図

【符号の説明】

1…強度測定治具

2…貫通穴部

【図 1】



フロントページの続き

【要約の続き】

【選択図】 なし